CATALYST ASSESSMENT FOR UPGRADING SHORT CONTACT TIME
SRC TO LOW SULFUR BOILER FUELS

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Introduction

Solvent refined coal (SRC) can be upgraded via catalytic hydroprocessing into low sulfur fuels (1,2). Reduced process cost can be effected by several factors, including the following: higher catalyst activity, improved utilization of hydrogen, and optimized SRC concentration in the feedstock. To this end, a series of commercial and proprietary catalysts was evaluated for the hydroprocessing of 50 wt % W. Kentucky short contact time SRC (SCT SRC). The commercial catalysts tested were alumina-based and were known to have good hydrotreating activity for heavy petroleum or coal-derived liquids. The rates of hydrogenation and pore size distribution will be discussed. A developmental catalyst with relatively high desulfurization and efficient hydrogen utilization was tested in a constant temperature aging run to establish process conditions needed to produce 0.4 wt % sulfur boiler fuels.

Experimental

The experiments were conducted in a continuous down-flow fixed bed pilot unit. The feedstock, 50 wt % W. Kentucky/SRC recycle solvent blend, was prepared in a charge reservoir and transferred to a weigh cell by gravity flow. Both the charge reservoir and weigh cell were kept at 350°F. After the reactor, hydrogen and light gases were separated from hydrotreated oil through high (300°F) and low (75°F) temperature separators in series. To maintain fluidity of the high SCT SRC concentration blend, all lines and valves from the charge reservoir to the high temperature separator were heat-traced to 340-420°F. The detailed description of the pilot unit is available elsewhere (1). The selection of SCT SRC as the feed was based on a recent finding that the hydrogen utilization efficiency for production of hydrogen-rich coal liquids can be improved by coupling mild short resident time hydroliquefaction (to produce SCT SRC) with catalytic hydroprocessing (3).

The catalysts were presulfided with a 10% H_2S/H_2 mixture and tested at a reactor pressure of 2000 psig and a hydrogen circulation of 5000 scf/B. Each catalyst was subjected to a standard sequence of temperatures and liquid hourly space velocities, ranging from 720-800°F and 0.5-2.0 hour^{-1}, respectively.

Results and Discussions

Fresh Catalyst Properties - Three Mobil catalysts were tested and have been identified as HCL-1, -2, and -3. Because of the proprietary nature of these catalysts, properties have been excluded. The major properties of the four commercial and two developmental catalysts are shown in Table 1. The four commercial catalysts evaluated were NiMo/Al$_2$O$_3$: Harshaw's 618X and HT-500, and American Cyanamid's HDN-1197 and HDS-1443. The NiMo catalysts were

tested in a greater number than the CoMo catalysts because it had been thought that improved hydrogenation activity was needed to treat the highly refractory SRC. Also, nickel-promoted hydroprocessing catalysts form less coke than cobalt-promoted catalysts, possibly resulting in better stability. The 618X, HT-500, and HDS-1443 catalysts all have similar metals loading; their major difference is found in surface area, going from relatively low to medium to high, respectively. The shift in surface area can also be seen in the different pore size distributions. Harshaw 618X has a well-defined distribution with 77% of its pore volume in the 100-200Å diameter region. HT-500 has a broader distribution and smaller median size, having half of its pore volume in the 80-100Å region. HDS-1443 has a bimodal distribution: it has most of its pores in 30-80Å, but it also has some 200Å$^+$ pores. HDN-1197 has a higher metals loading than the other NiMo catalysts and also has most of its pores in the 30-80Å region.

Two developmental catalysts were evaluated in this study. These include Amocat 1A and 1B, recently developed by Amoco for testing in the H-Coal ® Process (4). Both catalysts were made of the same support and had primarily 100-200Å pores with some macropores (>1000Å). Amocat 1B is an unpromoted Mo/Al_2O_3 while 1A is $CoMo/Al_2O_3$.

Fresh Activity Comparisons - The nine catalysts have been divided into two groups in order to simplify the activity comparisons. Group A is made up of the more active desulfurization catalysts and includes Mobil HCL-2, Mobil HCL-3, American Cyanamid HDS-1443, and Amocat 1A. Group B includes Mobil HCL-1, Harshaw 618X, American Cyanamid HDN-1197, and Amocat 1B. For the activity comparisons, the heteroatom removals (and CCR reduction) are plotted versus reactor temperature at a liquid hourly space velocity of 1.0. Consequently, catalyst activity can be compared on the basis of temperature requirements for achieving specific liquid product heteroatom (or CCR) contents.

The comparisons of desulfurization activities are shown in Figure 1 and Figure 2 for Group A and Group B catalysts, respectively. At the 80% desulfurization level, Mobil HCL-2 is 10-15°F more active than HDS-1443, followed by HCL-3, Harshaw 618X, and Amocat 1A (Figure 1). Surface area and pore size distribution seem to be important parameters for the fresh catalyst activity. The relatively high fresh activity of HDS-1443 may be partially explained by its high surface area and presence of macropores (Table 1). The presence of macropores may be responsible for the improvement of the relative positions of HDS-1441 and Amocat 1A at more severe conditions (0.5 LHSV).

The importance of pore size distribution also explains the low activity of HT-500, which has 75% of its pore volume in the 100Å region. Cyanamid HDN-1197 seems to have a high desulfurization activity (Figure 2). However, it yields an inhomogeneous product, probably due to its high hydrogenation activity coupled with its small pore size. Inhomogeneous products have also been observed in the upgrading of regular SRC by small pore catalysts (1). The SCT SRC, with its high polar asphaltenes content, is particularly susceptible to "front end, back end" incompatibility.

The ranking of deoxygenation activity was very similar to that of the desulfurization activity (Figure 3). The results may suggest that, like desulfurization, the deoxygenation reaction could occur without pre-hydrogenation. The comparison of denitrogenation activities is shown in Figure 4. Mobil HCL-3 was the most active catalyst followed by Mobil HCL-2 and Harshaw 618X.

The CCR reduction activity for the nine catalysts is similarly plotted as a function of temperature in Figure 5 and Figure 6. Mobil HCL-2, HCL-3, and Amocat 1B are the most active catalysts. Generally, heteroatom removal can be achieved with only minor changes in chemical structure. However CCR reduction in SCT SRC occurs with significant alteration of GEC classes, primarily toward the formation of less polar compounds. The classes of W. Kentucky SCT SRC, separated by GEC (gradient elution chromatography), are given in Table 2 and show that 75% of the SRC is polar and non-eluted polar asphaltenes.

Table 2: GEC Analyses of W. Kentucky SCT SRC

Saturates	0.3 wt %
Aromatic Oils	0.4 wt %
Resins/Asphaltenes	24.8 wt %
Polar Asphaltenes	45.1 wt %
Non-Eluted Asphaltenes	29.4 wt %
	100.0

The conversion of polar asphaltenes (lumped with non-eluted asphaltenes) as a function of process severity, expressed by hydrogen content in the liquid product, is shown in Figure 7. Amocat 1B and HDS-1443 show a significantly high conversion of polar asphaltenes at a given process severity. It is worth noting that Amocat 1B and HDS-1442, the Co-Mo version of HDS-1443, have been found to be active catalysts for coal hydroliquefaction (4).

Hydrogen consumption is a major economic factor in any coal liquid hydroprocessing operation. In Figure 8, the total hydrogen consumption is plotted vs. total liquid product (TLP) sulfur content. Three selectivity curves have been drawn from Figure 8: the solid curve represents Harshaw 618X, and the dashed curves are for Amocat 1A and 1B. To a rough approximation HCL-2, HDS-1443, and Amocat 1A are "low" hydrogen consumption catalysts; Harshaw 618X and Mobil HCL-3 are relatively "high" hydrogen consumption catalysts. At the same level of desulfurization Harshaw 618X uses approximately 500 scf/B more than Amocat 1A. However, Amocat 1B, a low desulfurization activity catalyst, shows a very high hydrogen consumption.

Analyses of Used Catalysts - The analyses of five used catalysts tested with 50% W. Kentucky SCT SRC are given in Table 3. The coke and iron depositions appear to be strongly dependent upon catalysts; Harshaw 618X and HDS-1443 are high, but Amocat 1A and 1B are low in coke deposition. Since surface area measurements can include contribution by contaminants (particularly coke), these values have no clearcut meaning. Besides the coke deposition, metal deposition on the catalysts contributes to the catalyst deactivation.

154

Table 3: Used Catalyst Properties as Received

	Harshaw 618X	Harshaw HT-500	Cyanamid HDS-1443	Amocat 1B	Amocat 1A
Surface Area, M^2/g	132	147	201	137	125
Pore Volume, cc/g	0.349	0.253	0.568	0.510	0.487
Pore Diameter, Å	106	69	113	149	156
Iron, Wt Pct	0.61	0.30	0.35	0.77	0.61
Coke, Wt Pct	20.6	23.0	18.0	12.8	13.0

The deposition of metal contaminants on a used Harshaw 618X catalyst
was analyzed with a scanning electron microscope (SEM). The SEM
x-ray emission spectra for fresh and used catalysts at different
locations in the catalyst particle are shown in Figure 9. The used
catalyst, tested after our standard procedure, showed a large
buildup of iron and titanium in a narrow band (<2 microns) of the
catalyst exterior. Other contaminants (e.g., K, Ca, Si) were
detected at lower concentrations. As shown in Figure 9(b), strong
intensities of deposited metals were clearly shown in the x-ray
emission spectrum taken near the extrudate external surface. The
intensities were substantially reduced in analyses made away from
the exterior edge, as shown in Figures 9(c) and 9(d). These results
indicate that the hydroprocessing of coal liquids is well suited to
ebullated bed reactors; the motion of the fluidized catalysts may
provide a continuous, partial regeneration by mildly abrading the
metals-rich pellet exterior.

Aging Run - Based on the fresh activity evaluation, Amocat 1A was
tested in an aging run for the hydroprocessing of 50% W. Kentucky
SCT SRC. The run was made at constant conditions (2000 psig, 775°F,
0.5 LHSV) and was smoothly operated for 15 days. The run was then
terminated due to incipient plugging in the reactor. The results
are shown in Figure 10, where sulfur content in the liquid products
has been plotted vs. days-on-stream. During this first four days
the temperature was varied to obtain an activation energy estimation,
and these data have been omitted.

A simple deactivation equation was used for a fixed bed reactor:

$$\frac{1}{C_A} - \frac{1}{C_{AO}} = \frac{k_o e^{-E/RT} e^{-t/\tau}}{LHSV}$$

where C_{AO} and C_A are the initial and final concentrations of
reactant (i.e., heteroatom or CCR). Here, k_o is the fresh pre-
exponential factor, LHSV is liquid hourly space velocity, E is
activation energy, T is reaction temperature, t is time on-stream and
τ is catalyst deactivation time constant. The estimated values for τ,
k_o, and E are as follows:

	k_o $\frac{1}{Wt\ \%-hr}$	E $\frac{Btu}{lb\ mole}$	τ Days
Sulfur	1.992×10^{13}	69,900	18.3
Nitrogen	3.368×10^{5}	34,600	36.1
Oxygen	6.895×10^{9}	57,800	8.9
CCR	2.553×10^{7}	50,400	21.9

The temperature rise necessary to maintain a constant product sulfur concentration is about 2-3°F/day. The measured and model-predicted values for sulfur and CCR are shown in Figure 10.

The simulated operating conditions for the fixed bed reactor to produce a 900°F+ fuel with a sulfur content of 0.4 wt % are shown in Figure 11, using a charge of 50% W. Kentucky SCT SRC. Figure 11 shows the reactor temperature required to achieve these sulfur levels as a function of days-on-stream and LHSV. The temperature rise is 2.5-3.0°F/day. The cycle length, a function of both LHSV and the limit of reactor temperature, can be determined from Figure 11. For example, at 0.3 LHSV and a maximum reactor temperature of 850°F, the cycle length is 60 days.

Conclusions

Short contact time SRC can be upgraded via catalytic hydroprocessing into low sulfur boiler fuels. However, the solid SCT SRC feedstock requires solvent dilution to reduce its viscosity. Furthermore, even for a 50 wt % W. Kentucky SCT SRC blend, all pilot unit lines and valves have to be heat-traced above 350°F in order to achieve smooth mechanical operations.

Catalytically, the SCT SRC is more susceptible to form an inhomogeneous product than the regular SRC, particularly where small pore catalysts are used. The upgrading costs can be significantly reduced through increased activity as well as efficient hydrogen utilization. A proprietary catalyst, Mobil HCL-2, and a developmental catalyst, Amocat 1A, were observed to have these two important properties. For hydroprocessing of the 50 wt % W. Kentucky SCT SRC blend, the aging rate was moderate with a 2-3°F/day of temperature rise required to keep constant desulfurization activity. The catalysts are believed to be deactivated by coke and metal depositions on the surface. A large buildup of iron and titanium was found in a narrow band of the catalyst exterior of a spent catalyst. Improved catalyst aging is likely to occur by the use of an ebullated bed reactor, primarily by decreased interparticle coke formation as well as by mild abrasion of metal contaminants.

Acknowledgement

Reference

(1) Stein, T. R., et al, Annual Report, EPRI Contract No. AF-873 (RP 361-2). Mobil Research and Development Corporation, December 1978.

(2) Givens, E. N., Collura, M. A., Skinner, R. W., and Greskovich, E. J., Hydrocarbon Processing, 195, November 1978.

(3) Mitchell, T. O., and Heck, R. H., Presented at AIChE 71st Annual Meeting, Miami Beach, Florida, November 13, 1978.

(4) Bertolacini, R. J., Gutberlet, L. C., Kim, D. K., and Robinson, K. K., Final Report, EPRI Contract No. AF-1084 (Project 408-1), Amoco Oil Company, June 1979.

Table 1

FRESH CATALYST PROPERTIES

	Harshaw 618X	Harshaw HT-500	Cyanamid HDN-1197	Cyanamid HDS-1443	Amoco* 1B	Amoco 1A
Compositions, Wt %						
Ni	2.7	2.4	3.7	2.9	0	
CoO						2.9
MoO_3	14.8	14.0	21.7	15.5	14.9	19.7
Physical Properties						
Surface Area, m^2/g	140	193	130	306	167	154
Pore Volume, cc/g	0.60	0.511	0.379	0.764	0.67	0.662
Pore Diameter, Å	172	104	117	100	160	172
Pore Size Dist., cc/g						
0 - 30Å	0.025	0.005	0.059	0.165 ⎫	0.027	0.065
30 - 80 Å	0.037	0.125	0.123	0.355 ⎭		0.046
80 - 100 Å	0.036	0.252	0.112	0.020	0.063	0.063
100 - 200 Å	0.464	0.123	0.035	0.033	0.419	0.385
200 A +	0.038	0.007	0.050	0.192	0.153	0.103

* Amoco's Analyses

Figure 1

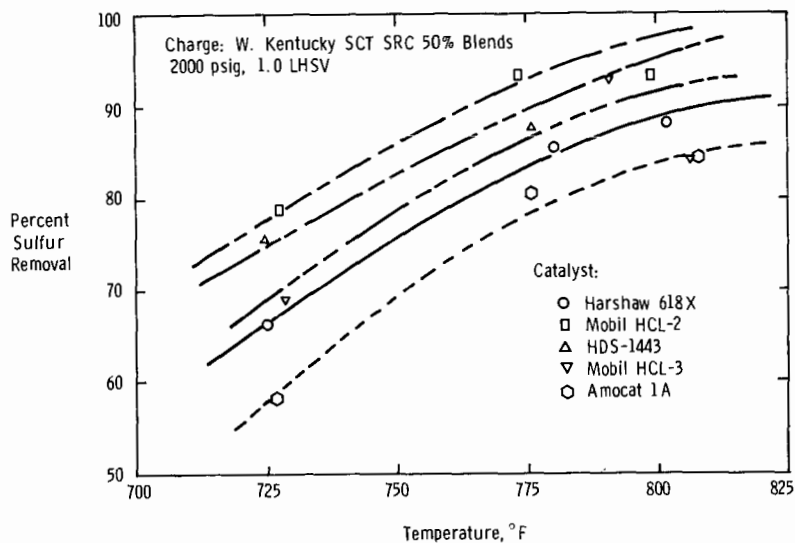COMPARISON OF DESULFURIZATION ACTIVITIES: GROUP A CATALYSTS

Charge: W. Kentucky SCT SRC 50% Blends
2000 psig, 1.0 LHSV

Percent
Sulfur
Removal

Catalyst:

○ Harshaw 618X
□ Mobil HCL-2
△ HDS-1443
▽ Mobil HCL-3
○ Amocat 1A

Temperature, °F

Figure 2

COMPARISON OF DESULFURIZATION ACTIVITIES: GROUP B CATALYST

Charge: W. Kentucky SCT SRC 50% Blends
2000 psig, 1.0 LHSV

Percent
Sulfur
Removal

Catalyst:

○ Harshaw 618X
□ HT-500
△ Mobil HCL-1
▽ Amocat 1B
○ HDN-1197

Temperature, °F

158
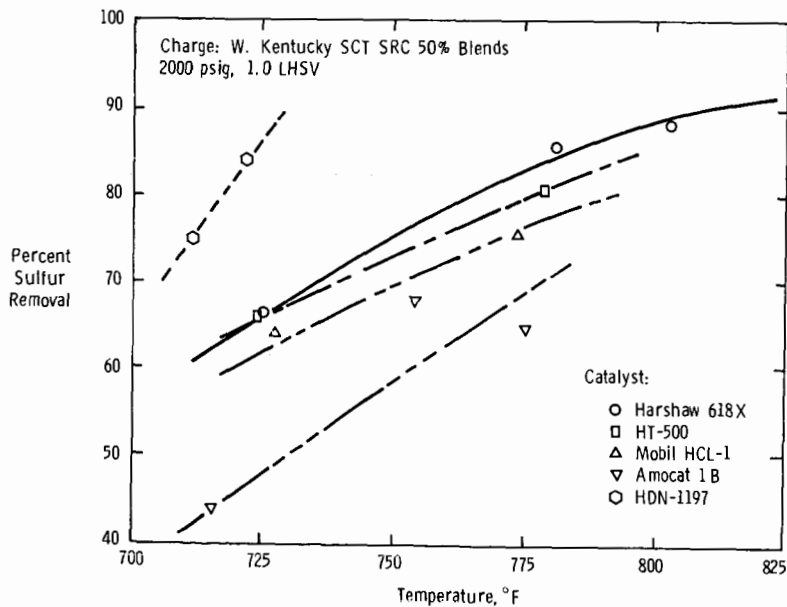
Figure 3

COMPARISON OF DEOXYGENATION ACTIVITIES: GROUP A CATALYSTS

Charge: W. Kentucky SCT SRC 50% Blends
2000 psig, 1.0 LHSV
Catalyst:

○ Harshaw 618X
□ Mobil HCL-2
△ HDS-1443
▽ Mobil HCL-3
○ Amocat 1A

Percent Oxygen Removal

Temperature, °F
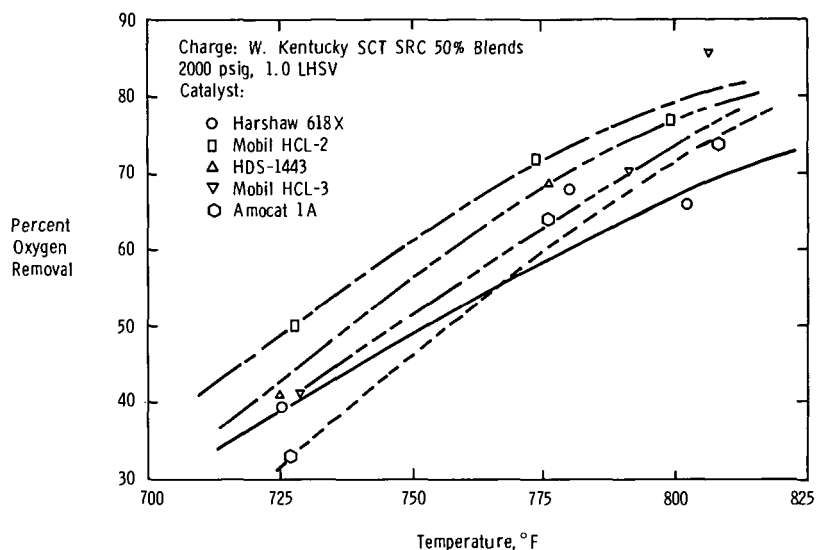
Figure 4

COMPARISON OF DENITROGENATION ACTIVITIES: GROUP A CATALYSTS

Charge: W. Kentucky SCT SRC 50% Blends
2000 psig, 1.0 LHSV
Catalyst:

○ Harshaw 618X
□ Mobil HCL-2
△ HDS-1443
▽ Mobil HCL-3
○ Amocat 1A

Percent Nitrogen Removal

Temperature, °F

159
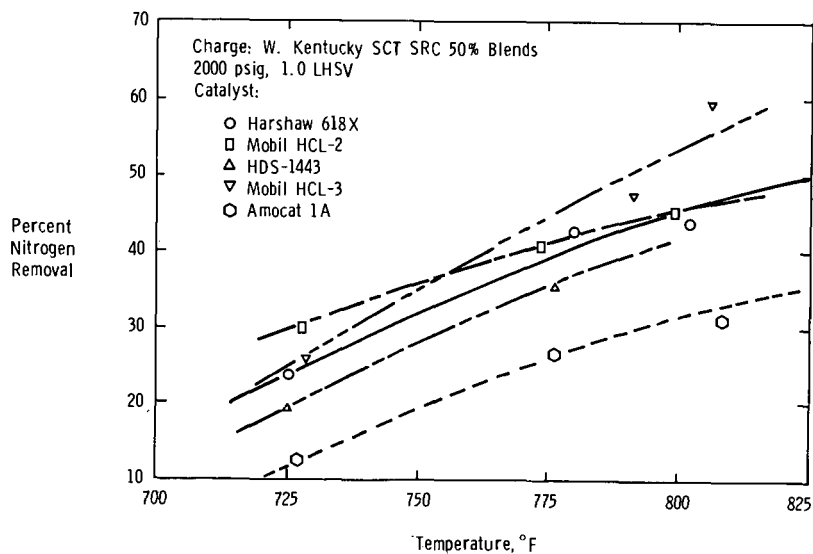
Figure 5

COMPARISON OF CCR REDUCTION ACTIVITIES: GROUP A CATALYSTS

Charge: W. Kentucky SCT SRC 50% Blends
2000 psig, 1.0 LHSV
Catalyst:

○ Harshaw 618X
□ Mobil HCL-2
△ HDS-1443
▽ Mobil HCL-3
◎ Amocat 1A

Percent CCR Reduction

Temperature, °F
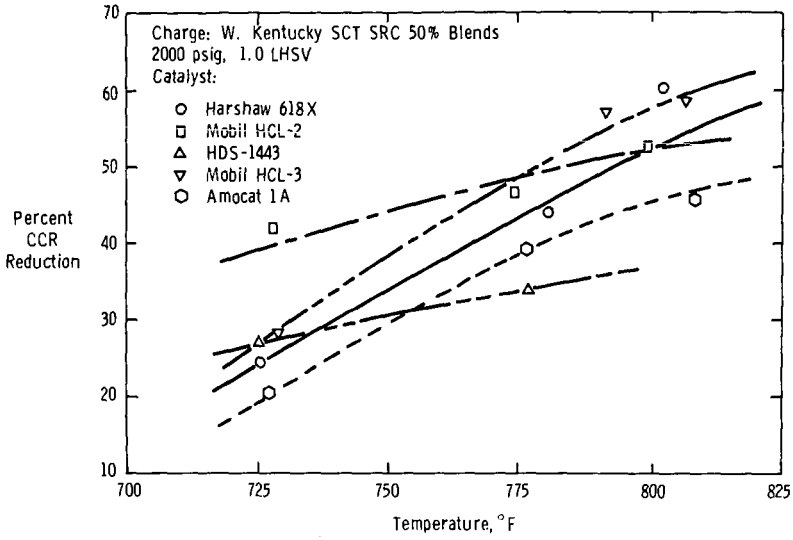
Figure 6

COMPARISON OF CCR REDUCTION ACTIVITIES: GROUP B CATALYSTS

Charge: W. Kentucky SCT SRC 50% Blends
2000 psig, 1.0 LHSV
Catalyst:

○ Harshaw 618X
□ HT-500
△ Mobil HCL-1
▽ Amocat 1B
◎ HDN-1197

Percent CCR Reduction

Temperature, °F

160
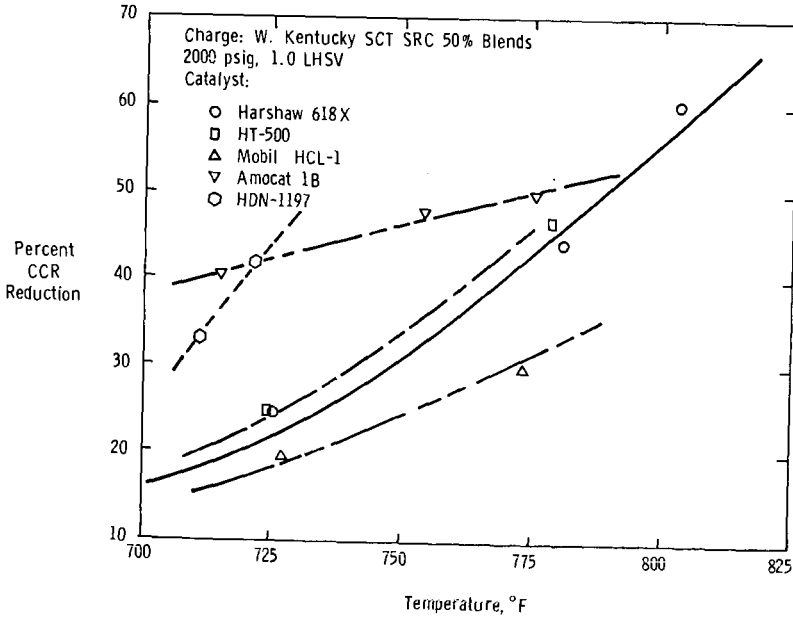
Figure 7

POLAR ASPHALTENES CONVERSION AS A FUNCTION
OF HYDROPROCESSING SEVERITY

Charge: W. Kentucky SCT SRC 50% Blend
Catalyst:

□ Harshaw 618X
△ Amocat 1B
▽ Mobil HCL-2
○ HDS-1443

Polar
Asphaltenes
in TLP,
Wt %
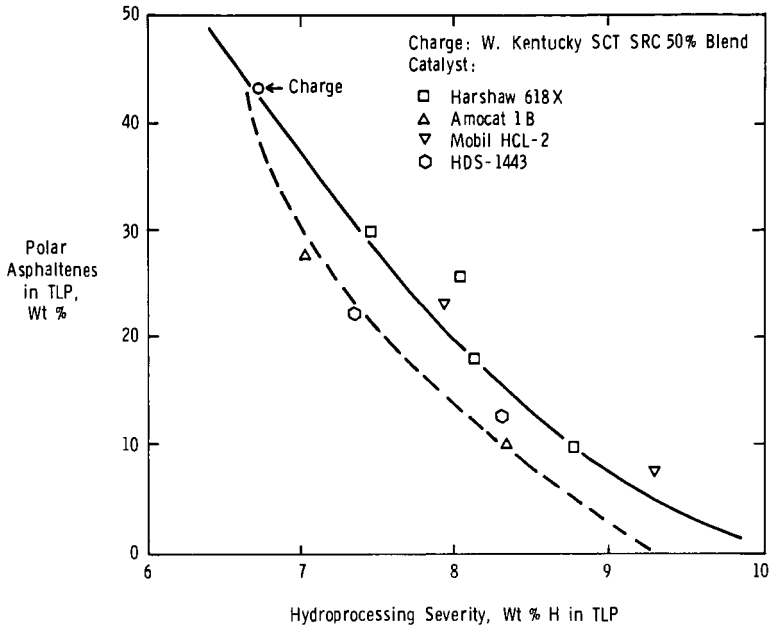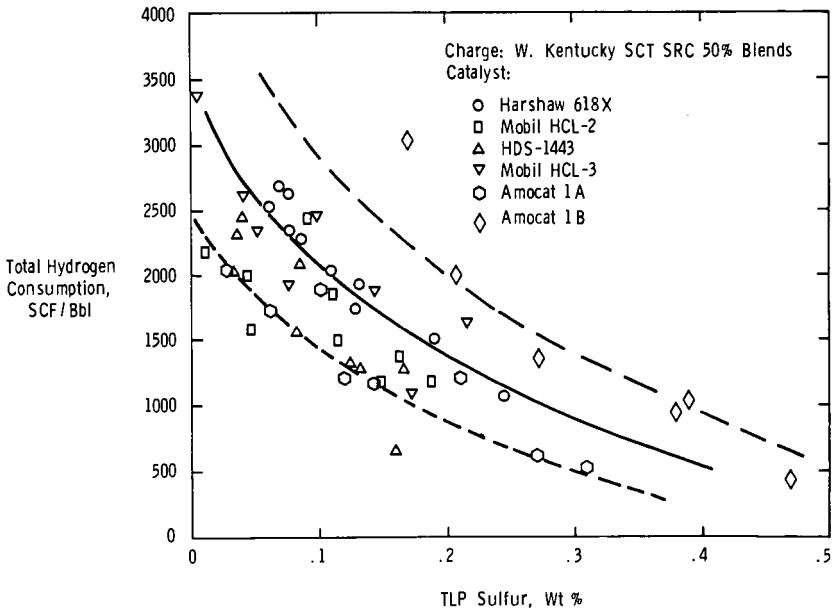
Hydroprocessing Severity, Wt % H in TLP
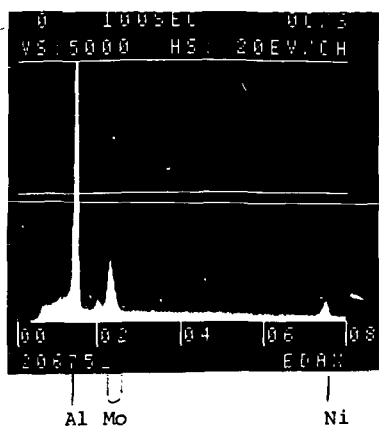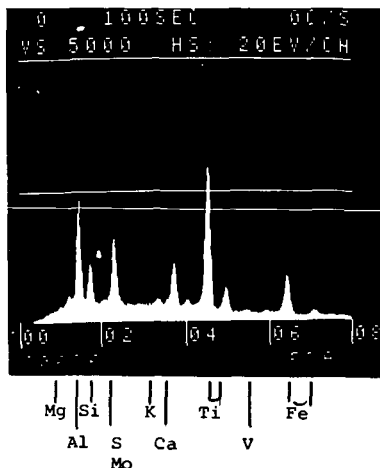
Figure 8

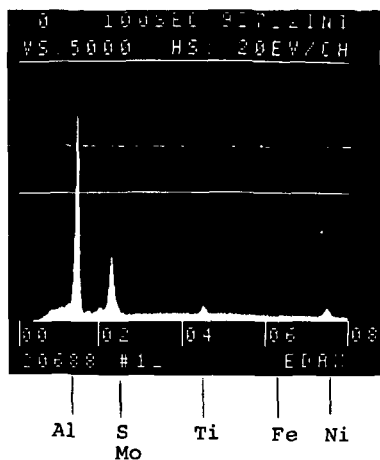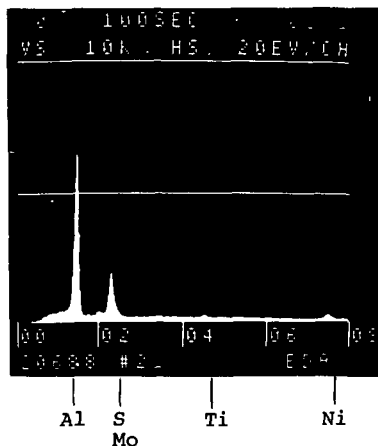TOTAL HYDROGEN CONSUMPTION AS A FUNCTION OF
SULFUR IN LIQUID PRODUCT

Charge: W. Kentucky SCT SRC 50% Blends
Catalyst:

○ Harshaw 618X
□ Mobil HCL-2
△ HDS-1443
▽ Mobil HCL-3
○ Amocat 1A
◇ Amocat 1B

Total Hydrogen
Consumption,
SCF / Bbl

TLP Sulfur, Wt %

161

FIGURE 9:   SEM Examination of Fresh and Used Harshaw 618X

(a) X-ray emission spectrum taken of external surface of fresh catalyst
    showing presence of Al, Mo and Ni.

(b) X-ray emission spectrum taken of external surface of used catalyst
    showing presence of Mg, Al, Mo, K, Ca, Ti, V and Fe.

(c) X-ray emission spectrum taken at 0-20 μ from the edge of the cross
    section of used catalyst showing presence of Al, Mo, Ti, Fe and Ni.

(d) X-ray emission spectrum taken at 60-80 μ from the edge of the cross
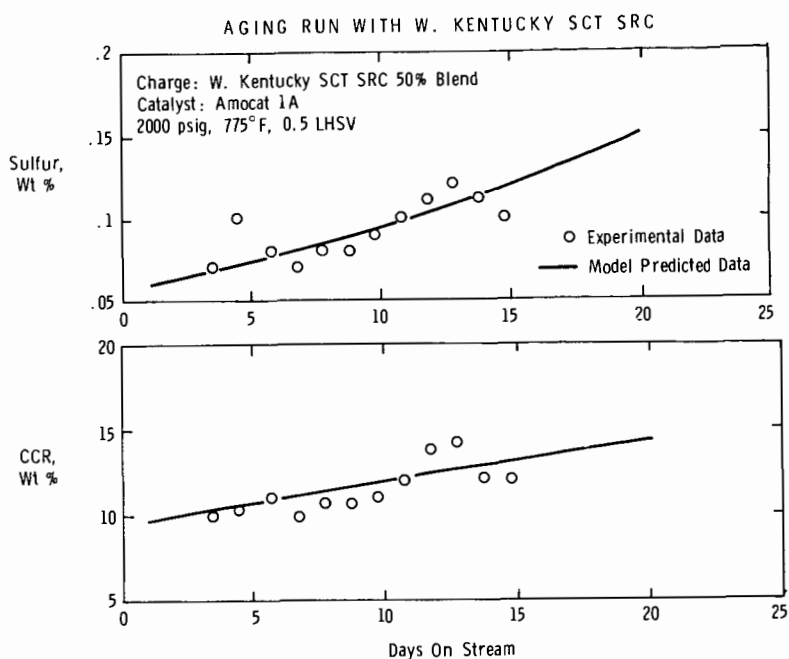   section of used catalyst showing presence of Al, Mo, Ti and Ni.

Figure 10

AGING RUN WITH W. KENTUCKY SCT SRC

Charge: W. Kentucky SCT SRC 50% Blend
Catalyst: Amocat 1A
2000 psig, 775°F, 0.5 LHSV

Sulfur, Wt %

○ Experimental Data
— Model Predicted Data

CCR, Wt %

Days On Stream

Figure 11

DESIGN VARIABLES FOR FIXED BED REACTOR

Charge: W. Kentucky SCT SRC 50% Blends
Catalyst: Amocat 1A

Product Sulfur Concentration:
0.15 Wt % in TLP
0.4 Wt % in 900°F $^+$

0.5 LHSV
0.3 LHSV
0.1 LHSV

Reactor Temperature, °F

Days On Stream

163